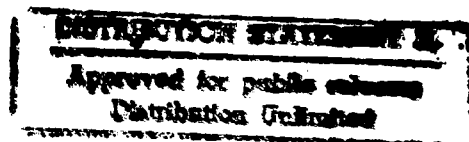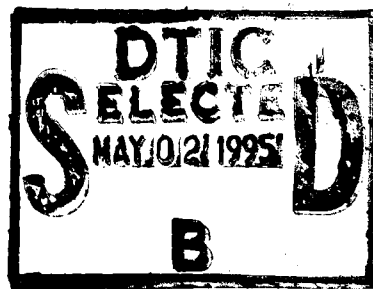SPECIAL REPORT

Incorporation of Crude and Fuel Oil into Salt- and Freshwater Ice

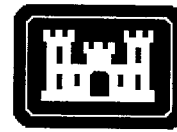Susan Taylor and Nancy Perron   February 1995

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Abstract

North Slope Crude, no. 2 fuel oil, and vegetable oil were each released under columnar freshwater and saltwater ice grown in a laboratory coldroom. Because the thermal conductivity of all the oils is lower than that of water or ice, thinner ice grew under the oil and resulted in a concave ice/water interface. Both the fresh and saline ice encapsulated the oils, but the saline ice did so more slowly. Thin sections of the ice blocks containing the crude and fuel oils show how the columnar ice crystals bend around and under the oil patches. The movement of the vegetable oil during melting was photographed, and spectral reflectance measurements of the ice surface were made to determine if the oil could be detected remotely. Although we could detect the presence of oil under 10 cm of ice, under field conditions the optical detectability of oil will depend upon the depth of the oil within the ice, the type of ice, and the contrast between the under-ice oil and the background against which it is being viewed.

Special Report 95-6

**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

Incorporation of Crude and Fuel Oil into Salt- and Freshwater Ice

Susan Taylor and Nancy Perron

February 1995

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PREFACE

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Incorporation of Crude and Fuel Oil
into Salt- and Freshwater Ice

SUSAN TAYLOR AND NANCY PERRON

INTRODUCTION

Oil drilling on the Arctic continental shelf and transportation of oil through cold waters results in oil spills into ice-covered and icy waters. Information on the behavior of oil in icy water and under and within different types of ice is needed to determine the fate of the oil and to select clean-up options.

Oil spilled in cold water does not spread as rapidly as it does in temperate waters, due to the oil's greater viscosity at lower temperatures, and if ice floes are present they can serve as "booms" and contain the oil (Wolfe and Hoult 1974, Greene et al. 1977, Wheeler 1978). Even so, cleaning up oil spilled in icy waters presents many difficulties. The effectiveness of various clean-up methods in ice-infested waters were assessed when an accident spilled 306.5 cubic meters (81,000 gallons) of no. 2 fuel oil into Buzzards Bay, Massachusetts, in January 1977 (Ruby et al. 1977). The section of the bay affected was 90% ice-covered at the time, with ice ranging in thickness from 15 to 45 cm. The researchers found that booms, skimmers, and sorbent pads were not very effective. Burning the oil and suctioning it off were found to be the most effective means of removing the oil.

When the oil is on the water surface, burning works well because the volatile fraction of the oil is not lost as quickly in cold temperatures, and, when present, ice floes dampen wave action that can disperse the oil. If the oil is spilled under the ice, it can still be burned when it surfaces (provided it forms a thick enough layer to sustain combustion), as it does not weather or emulsify significantly when under or in ice (Greene et al. 1977). An oil thickness greater than 0.5 cm was found to burn well, reducing the oil volume by 80% (Greene et al. 1977).

The effects of igniting an oil spill were studied in 1993 off the coast of Newfoundland. A 98.4-m^3 (26,000-gal) experimental oil spill was ignited. Results indicate that 90–98% of the oil was removed by burning, with the smoke accounting for 6–13% of the mass of the oil spilled (Raloff 1993).

The effect of the black oily smoke on the albedo and melt rate of the ice needs to be understood if burning is to be used as a remediation technique in ice-filled waters. Compounds such as ferrocene are being investigated as ways of decreasing the quantity of smoke produced (Raloff 1993).

Various studies have looked at how oil becomes incorporated into ice. Using North Slope crude and diesel fuel, Wolfe and Hoult (1974) made laboratory measurements to determine if oil spilled under saltwater ice would:

1) be encased in ice as the ice continued to form under the oil layer;
2) be moved ahead of the freezing front by the growing ice;
3) form an ice–oil mixture.

Their tests showed that the oil becomes encased in the ice and is not pushed in front of the freezing front or distributed within the ice. In their experiments a 1- to 2.6-cm-thick layer of oil covered the entire 30-cm^2 bottom of their ice block. They observed that small-grained, randomly oriented transition ice formed under the oil. The small amount of oil taken up by, or adhering to, the underside of the ice was found in the basal skeletal layer of the ice (Wolfe and Hoult 1974). Field experiments also show that only a small amount of oil is incorporated in the ice; the most oil-saturated sea ice was no more than 5% oil by volume (Martin 1979).

Field studies where crude oil was purposefully spilled under multiyear sea ice (Norman Wells, Canada) show that, over time, the oil moved vertically and horizontally within the ice and that the porosity of the ice was the key factor controlling its upward migration (Comfort and Purves 1982). Because brine channels are the main conduits through which oil moves, and because the number of brine channels increases and their spacing decreases as the ice warms (Martin 1979), oil migrates to the surface of the ice when the ice warms and begins to rot.

The absence of brine channels and the lower porosity of freshwater ice cause it to have a differ-
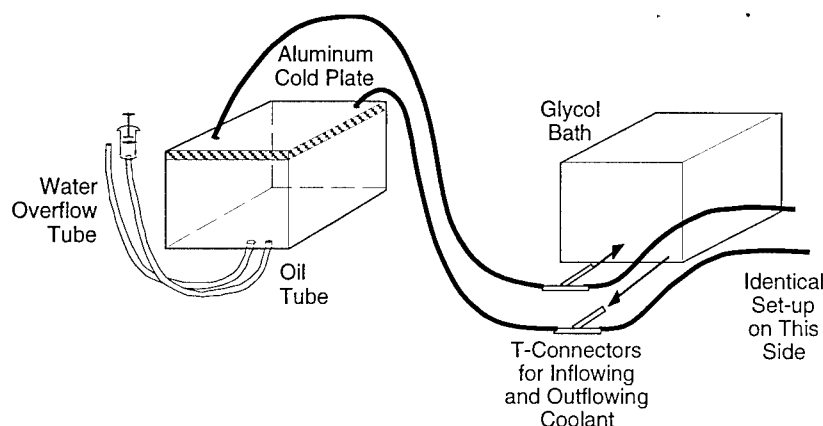
Figure 1. Experimental set-up.

ent interaction with oil than does saltwater ice. Experiments where Alberta crude was released in an ice-covered test pond showed that the oil exhibited nonwetting behavior and occurred as droplets or patches. Cracks were the pathways by which oil reached the surface (Greene et al. 1977).

All but the heaviest crude oils are less dense than ice. How and when the oil migrates to the ice surface has important consequences for the local heat balance of the area. The lower albedo of oil-stained ice promotes local melting, which allows more oil to surface (Beaufort Sea Project 1975). It has been argued that the presence of oil between and on the Arctic pack ice could cause large areas of pack ice to melt and could change the heat balance of the Arctic sea (Campbell and Martin 1973), but the importance of a large oil spill on the Arctic heat balance was disputed by Ayers et al. (1974).

In this report we describe some experiments where North Slope crude, no. 2 fuel oil, and vegetable oil were released under columnar freshwater and saltwater ice grown in a laboratory coldroom. The ice under which vegetable oil was released was taken outdoors and allowed to melt.

The movement of the oil during melting was photographed, and spectral reflectance measurements of the ice surface where made to determine our ability to detect the oil remotely. The vegetable oil was detectable at all depths in our experimental setup. Instead of making reflectance measurements of the ice containing the fuel and crude oil, we made thin sections of the ice, which allowed us to see how the oil changed the crystal structure of the ice growing around and under it.

MATERIALS AND METHODS

Columnar ice was grown because it is the primary type of crystalline ice texture found in Arctic sea ice and in freshwater bodies. Two 30-cm-wide by 40-cm-long by 30-cm-high Plexiglas ice growth boxes (see Fig. 1) were built. One box contained tap water, the other a 15 parts per thousand (ppt) aqueous solution of Morton Purex salt (because this is a closed system, the water becomes progressively more saline as salt is rejected from the ice). Both growth chambers were cooled by aluminum

Table 1. Experimental parameters used in the four tests.

| | | | Amount of oil released (cc) | | Ice thickness | | | | Temp-erature (°C) | |
| | | | | | When oil released (cm) | | At end of experiment (cm) | | | |
Test	Date	Oil type	Fresh	Salt	Fresh	Salt	Fresh	Salt	Plate	Room
1	April	100% vegetable	~167	170	16	~16	22	~20–24	–10	–2.2
2	July	100% vegetable	143	140	10.5	~7	20	~8–25	2 & –5	–2.2
3	Sept	No. 2 fuel oil	135	127	8.5	~7.5	20	~18	–5	–2.2
4	Nov	North Slope crude	140	140	14.5	14	20–23	14–23	10 & –5	–2.2

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Table 2. Thermal conductivity (W m^{-1} K^{-1}) of ice, water, oil, and air.
Note that the thermal conductivities of solids are higher than those of liquids,
which are in turn higher than those of gases.

Air	0.026	*CRC Handbook of Chemistry and Physics* (Lide 1991–92), 300°K
Crude oil	0.13	Wolfe (unpublished)
Motor oil	0.15	*Fundamentals of Heat Transfer* (Incropera and Dewitt 1981)
Water	0.56	*CRC Handbook of Chemistry and Physics* (Lide 1991–92)
Sea ice	1.3–2.1	Yen (1981), 273–253°K
Ice	2.2	Yen (1981), 273°K

cold plates that served as the top of each box. The cold plates were connected to the same glycol bath by tubing running from the inflow and outflow spigots on each cold plate to a T connector on the inflow and outflow of the glycol bath. The Plexiglas boxes each had two outlets in the bottom to which the tubing was connected. One outlet was a water overflow port and the other was used to release the oil under the ice. The oil was discharged under the ice using a 60-cc syringe modified to fit snugly onto the end of the tube connected to the oil injection port. The tubing running from both of the ports was wrapped with heat tape and insulated. The sides and bases of the boxes were insulated with black Armourflex. The glycol bath was set at –5°C and the room was maintained at –2.2°C.

This set-up resulted in a horizontal freezing front and produced 1 to 2 cm of transition ice followed by columnar ice. The total ice growth in the tanks was between 10 and 25 cm, an order of magnitude thinner than typical first-year sea ice (Martin 1979) and thinner than most pond ice growing in high latitudes. The freshwater ice had a well defined ice/water boundary, whereas the saltwater ice had a feathery interface produced by skeletal crystals growing in the supercooled brine.

Spectral reflectance measurements were made of the ice surface using an Analytical Spectral Device spectroradiometer. By dividing the reflectance of the ice surface by that of a standard, the spectral reflectance of the ice in the 0.4–1.0 micrometer range was measured.

TESTS AND RESULTS

A total of four tests were run. For each test a fresh- and a saltwater ice cover was grown. In the first two tests, vegetable oil was released under the ice. In tests 3 and 4, no. 2 fuel oil and North Slope crude were used, respectively. The parameters for the four tests are listed in Table 1. In all these tests, because the thermal conductivity of oil is an order

of magnitude less than that of salt- or freshwater ice and also smaller than the thermal conductivity of fresh water (Table 2), the ice that formed below the oil displayed a concave bottom topography.

Test 1

Vegetable oil was released under the fresh- and saltwater ice when each was about 16 cm thick. (The position of the oil in the cloudy brine ice was estimated by looking up through the salt water to the underside of the ice). As the oil cooled it solidified and changed from being translucent and yellow in color to an opaque, white, gelatinous-like material. Ice continued to grow around and under the oil. When the total ice thickness was about 22 cm in both tanks, the cold plates were removed from the top of the tanks and the tanks were placed outdoors. The sides of the two containers were kept insulated so that sunlight would not enter from the sides and to favor melting from the surface downward. The 24-hour average temperature was 5.9 ±5°C, and the ice took 3 days to melt. Melting occurred primarily from the top down, but the bottom and sides of the ice block also melted back (Fig. 2 and 3).

The series of photographs in Figure 2 shows two layers of vegetable oil in the freshwater ice. The second layer formed when oil, remaining in the oil release tube, was accidentally released into the tank. Soon after setting the block outside, the funnel-shaped ice under the top oil layer became sufficiently porous to allow the bottom oil layer to move up to the undersurface of the solidified top oil layer. Over the course of three days, as the ice melted, the top oil layer changed from a circular flat disk connected to the concave ice/water interface via a funnel-shaped opening (Fig. 2 top left) to an irregular disk at the ice/water interface (Fig. 2 bottom right). Ice 'lips' were observed to 'wrap' around the base of the oil (Fig. 2 bottom right).

How the oil behaved in the saltwater ice is not clear from the photographs (Fig. 3). The salt- and freshwater ice blocks melted at similar rates, and
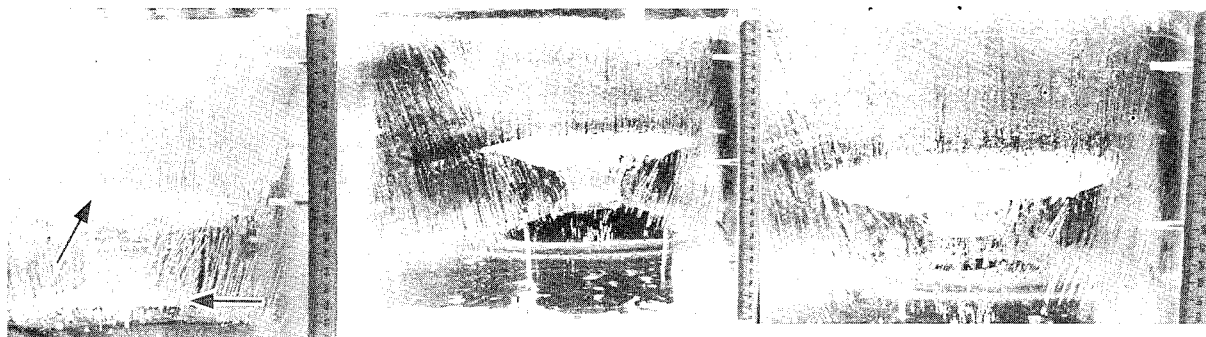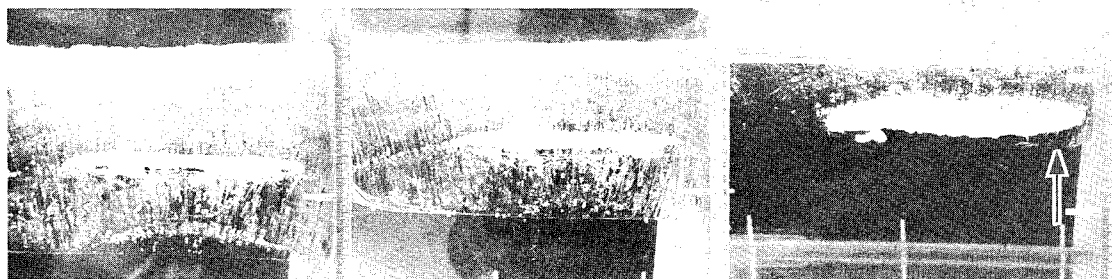
Figure 2. The melting of freshwater ice containing two layers of vegetable oil, indicated by the arrows in the lefthand photo of (a). Note the formation of a lip of ice (arrow) under the oil in (b).

oil appeared on the ice surface and in the surrounding water at approximately the same time in both tanks. These observations suggest that the saltwater ice did not release the oil appreciably faster than did the freshwater ice.

As the ice warmed, the boundaries between the individual ice crystals etched out and ice crystals began to separate from one another (Fig. 4). The vegetable oil, which had solidified, had the effect of keeping the ice crystals together so that at the end of the experiment, in both the fresh- and saltwater tanks, the only patches of ice left were those over the oil (Fig. 5).

Reflectance measurements were made every half hour between 10 a.m. and 2 p.m. during the three days that it took the ice to melt. All three days had clear skies. The results indicate that the ice over the oil had a higher reflectivity (10–20%) than the ice
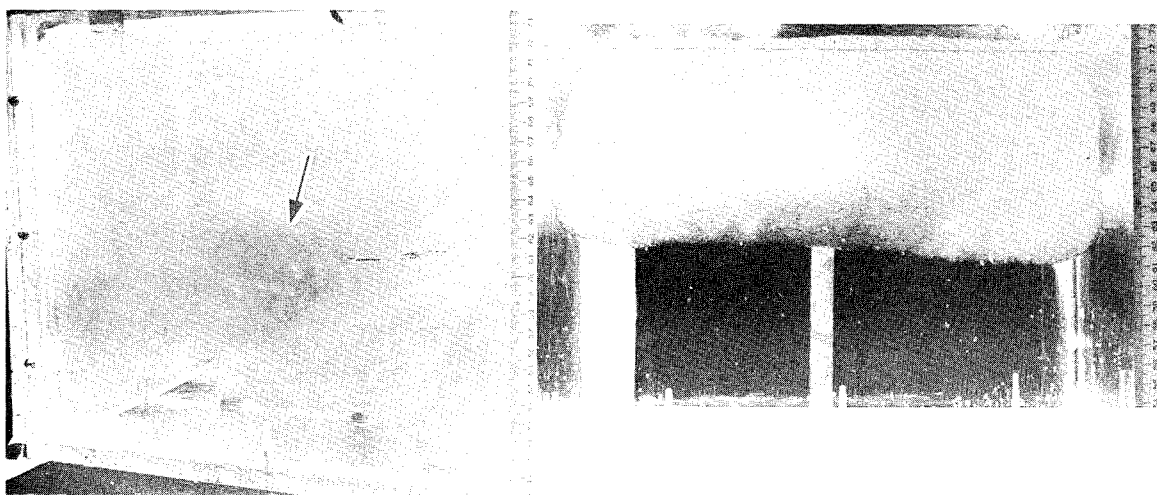

Figure 3. Saltwater ice with a vegetable oil layer.

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Figure 4. Ice crystals in the freshwater tank break away from each other as their grain boundaries melt (candle ice).

adjacent to it (5–10%). Unfortunately, the pink styrofoam insulation can be detected in these spectra. This situation was corrected in all subsequent tests by using black, nonreflective Armorflex.

Test 2

Vegetable oil was injected into the tanks after 8 cm of ice growth. In the fresh water tank, an additional 5 cm of ice grew directly below the oil and 12 cm of ice grew around the periphery of the oil. The ice thickness in the saltwater tank was asymmetrical, and the oil collected in a corner of the tank, not in the middle as in the previous test.

The 24-hour average temperature was much higher (22 ±4.9°C) than during test 1, and 2 hours after setting out the tanks, small amounts of oil had worked their way along bubble tracks to the surface in both tanks. Perhaps because of its proximity to the edge of the tank or possibly because the oil had been heated by solar radiation, the ice over the oil in the saltwater tank melted after 3 hours. Figure 6 shows how the grain boundaries in the freshwater ice etched out between 10 a.m. and
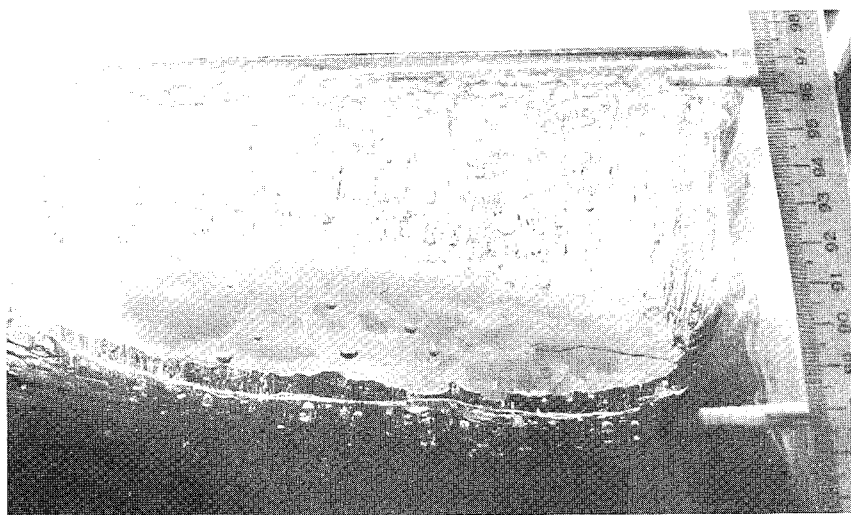

Figure 5. The cold, viscous oil kept the candled ice from falling apart.
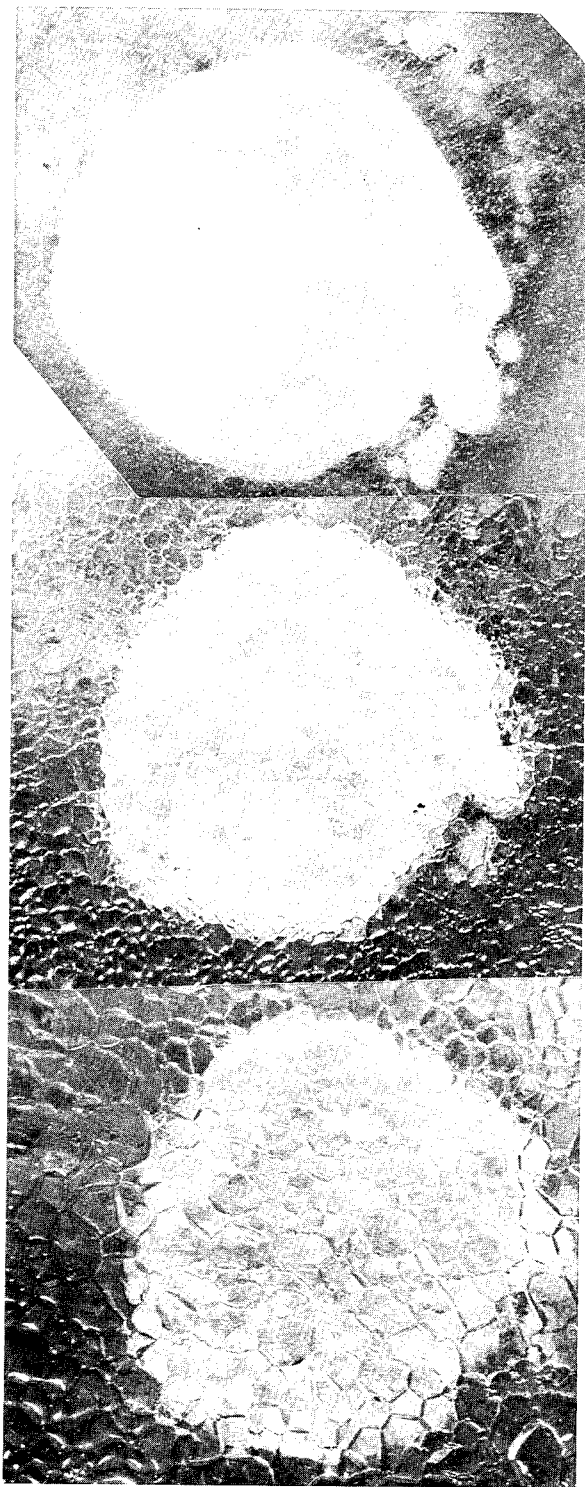
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Figure 6. Vegetable oil viewed through 8 cm of freshwater ice. Changes in the surface structure of the ice, caused by melting along the ice's grain boundaries, are apparent in this sequence of photographs.
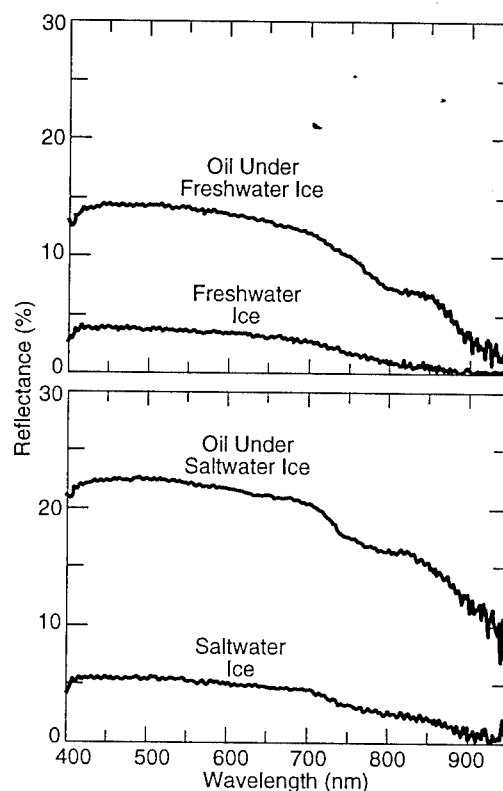

Figure 7. Spectral reflectance measurements of fresh- and saltwater ice and of vegetable oil under these two ice types (0.4–1.0 μm, 400–1000 nm).

noon. By 3:30 p.m. there was only 1 cm of ice over the oil in the freshwater tank. Instead of keeping the ice crystals together, as it had in test 1, the oil hastened melting. The section of ice over the oil broke away from, and was depressed relative to, the surrounding ice. By the following morning the ice in both tanks had melted. During this experiment the ice melted predominantly from the top down.

The day on which the tanks were taken outside was cloudless. Spectral reflectance measurements of the ice and ice over oil are similar to those obtained during the first test. The ice reflectance over the oil was higher (10–20%) than that of the ice itself (about 5%). The saltwater ice had a higher reflectance than the freshwater ice (see Fig. 7). The difference in reflectance caused by the presence of oil under the ice is visually apparent in photographs of the freshwater ice surface (Fig. 6).

Test 3

Number 2 fuel oil was released under 6 and 9 cm of salt- and freshwater ice, respectively. The oil

Figure 8. Thin sections showing the effect of no. 2 fuel oil on the growth of freshwater ice.

rose to the underside of the ice in centimeter-sized oil droplets. Unlike the vegetable oil, the fuel oil did not solidify but remained liquid throughout the course of the test. Five days after the oil was released, an additional 10 cm had grown under the freshwater ice and about 2 cm directly below the oil in the saltwater block, and the ice blocks were removed from the growth chamber. No reflectance measurements were made of the fuel or crude oils because the tests using the vegetable oil demonstrated that the oils would be detectable. Instead we looked at the crystal structure of the ice as it encapsulated the oil.

Thin sections of the freshwater ice showed that the columnar crystals were only slightly affected on each side of the oil but that under the oil layer the crystal orientation had changed (c-axis is vertical, measured at 95° relative to the c-axis in the vertically growing crystals). The crystals grew horizontally under the oil (Fig. 8). In the saltwater ice sections, the ice crystals grew around the oil layer (Fig. 9). The oil's position in the fresh- and saltwater ice are shown in Figure 10a and b, respectively.

Test 4

North Slope crude oil was injected under about 14 cm of fresh- and saltwater ice. The oil formed discrete droplets about 2 cm in diameter and about 0.5 cm thick. Under the freshwater ice the oil did not coalesce into a circular patch, as the fuel oil did, but remained as a ring of droplets (Fig. 11). Under the saltwater ice the oil spread laterally, over a larger area, as a layer of smaller droplets.

Four days after the oil was released, an additional 6–8 cm of ice had grown in the freshwater tank; there were 10 cm of ice near the edges of the saltwater tank but hardly any new ice under the oil (see Fig. 12a and b). The columnar crystals bent around the oil in the freshwater ice (Fig. 13) and the ice surface was concave at the ice/water interface. Small amounts of oil entered some of the bubble trails directly above the oil, but basically the oil stayed where it had been deposited.

Little information on crystal growth around the oil was obtained from thin sections prepared from the saline ice (Fig. 14) because there was very little ice under the oil. Where small (<0.5 cm) blobs of oil resided, the columnar ice crystals grew around the

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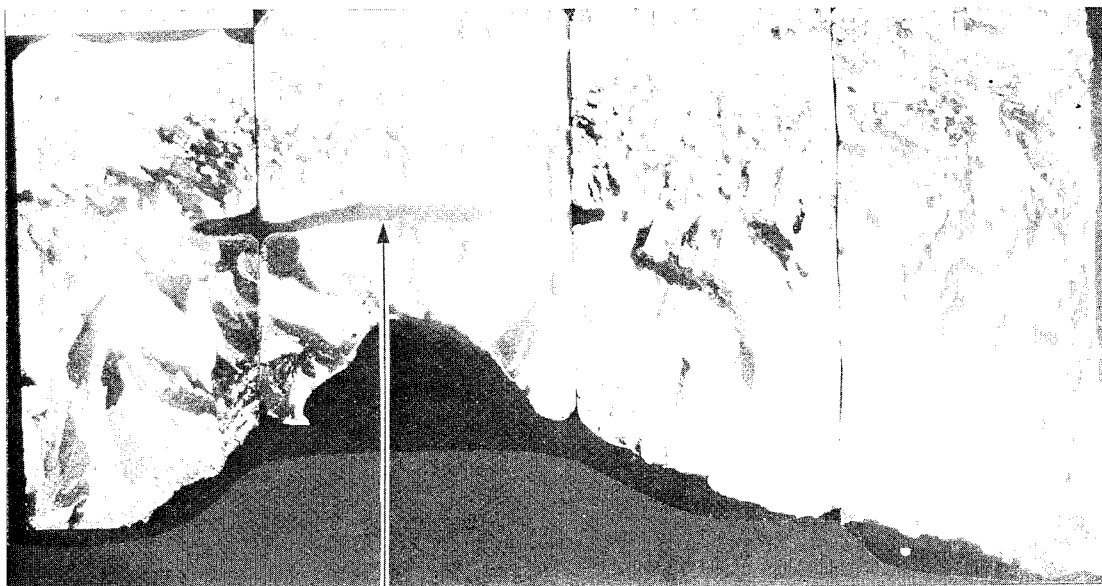*Figure 9. Thin sections showing the effect of no. 2 fuel oil on the growth of saltwater ice. Note the dramatic change in crystal structure below the oil.*
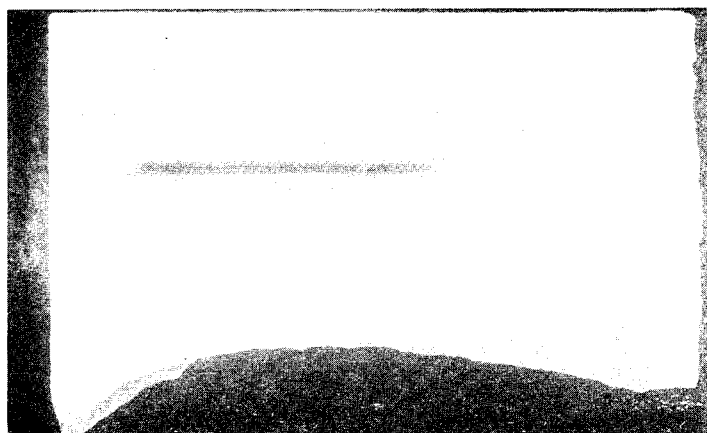
a. Freshwater block.
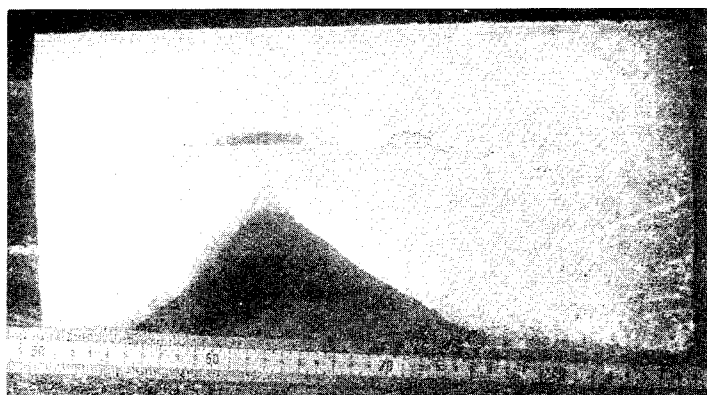
b. Saltwater block.

Figure 10. Ice blocks at end of the fuel oil experiment. The greater curvature of the ice/water interface under the oil in the saltwater block is due to the lower thermal conductivity of saline ice.

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Figure 11. Droplets of crude oil in a freshwater ice block.
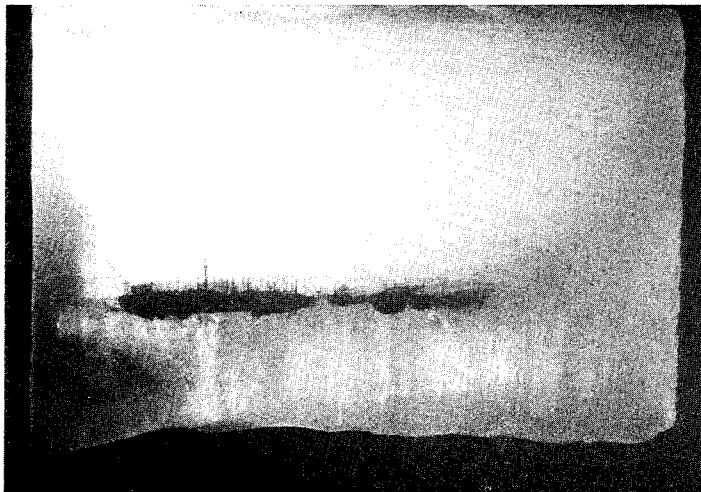
a. Freshwater block.

b. Saltwater block.

Figure 12. Ice blocks of (a) fresh and (b) salt water that contained crude oil.

Figure 13. Thin sections showing a crude oil layer encased in freshwater ice.

Figure 14. Thin sections showing crude oil in saltwater ice. The small-diameter blobs of oil intersected in these sections did not alter the crystal growth of the ice.

oil droplets without altering the crystal orientation (Fig. 14).

CONCLUSIONS

These experiments all showed the effect of oil's lower thermal conductivity on the growth pattern of both freshwater and saline ice. Oil has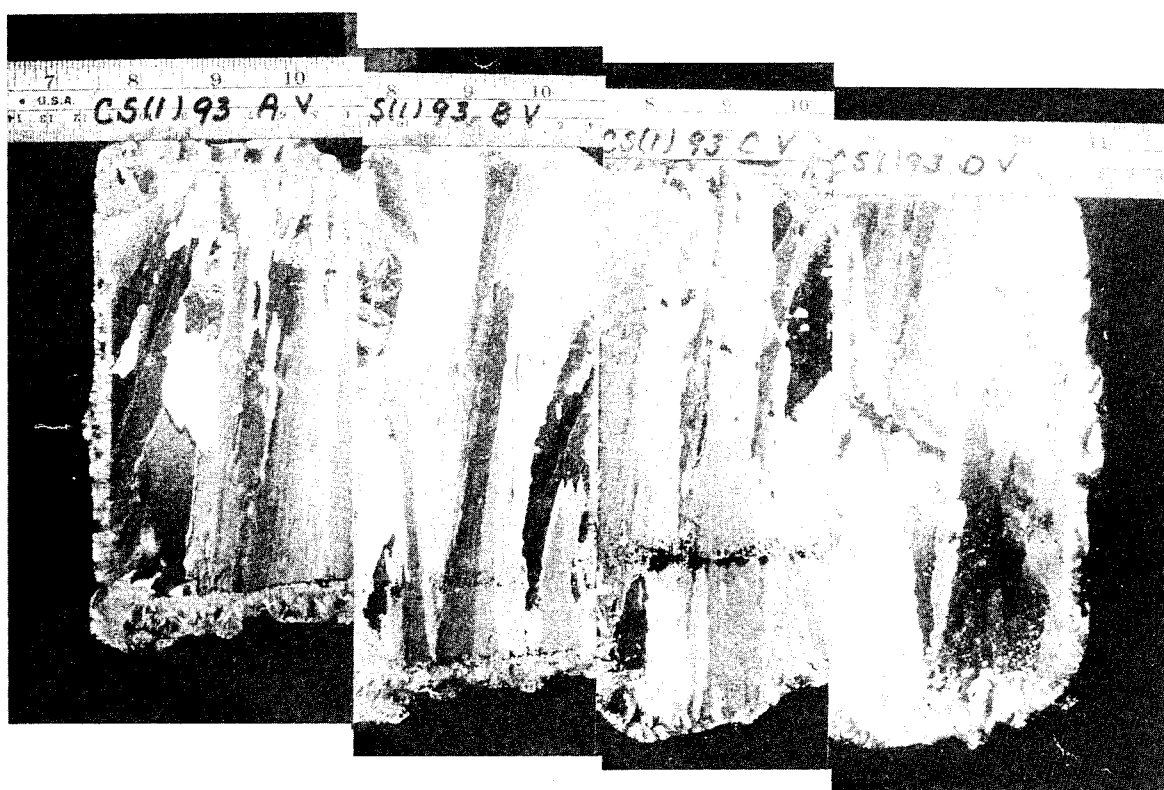 a thermal conductivity that is an order of magnitude lower than that of fresh or saline ice. This conductivity difference caused the ice crystals to grow around the oil and form a funnel-shaped ice growth area under the oil. This ice is thinner and more porous than the surrounding ice and results in a concave ice/water interface. The concavity is more pronounced in the saltwater ice than in the freshwater ice, possibly because the freezing rate is slower in salt water.

The underside of natural sea ice has an undulating surface that offers a large storage potential for any oil spilled under the ice (Kovacs et al. 1981). The oil should collect in concavities, both because of its buoyancy and because, once in the recess, it is not as easily transported by near-surface currents. The presence of the oil would accentuate this concave shape by retarding the growth of ice under the oil relative to the surrounding ice. This mechanism would tend to benefit oil clean-up operations as it would help to further contain the oil. Recesses in undersea ice result from thinner ice in these areas and are often due to the insulating effect of an overlying snow cover. The presence of a snow cover would preclude the remote detection of oil under ice.

The spectral reflectance measurements showed that the vegetable oil, which was light colored, was visible 12 cm under the surface of our laboratory ice. Because the tanks were insulated with black, nonreflecting Armorflex, the contrast between the ice over the dark bottom and the ice over the light-colored oil was good. In the field, the optical detectability of oil in ice is going to depend upon the depth of the oil within the ice, the type of ice (the path length of light in saline ice, which contains brine pockets, will be less than in freshwater ice), and the contrast between the oil and the background against which it is being viewed. A different experimental set-up is needed to determine the depth at which a par-ticular oil could be detected for different ice conditions.

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13. ABSTRACT (*Maximum 200 words*)

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14. SUBJECT TERMS

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Oil under ice	Spectral reflectance	

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